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Increasing the stability of membrane-electrode assemblies based on Aquivion[®] membranes under automotive fuel cell conditions by using proper catalysts and ionomers

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ABSTRACT

The large-scale application of polymer electrolyte membrane fuel cells (PEMFCs) requires a reduction of the costs and an improvement in performance and stability. Particularly, the automotive market needs the PEMFC works under harsh conditions (high temperature, low relative humidity, etc.), maintaining a good performance level and low degradation. These operating conditions permit to mitigate the constraints concerning the thermal and water management allowing both a simplification and a volume reduction of the system inside the car with a strong impact on costs and reliability. However, PEMFCs require the development of the components such as catalysts, ionomers and membranes with a proper stability.

In this work, PtCo/KB and Pt/KB electrocatalysts were investigated with the aim of verifying the performance and stability, coupling them with an innovative reinforced Aquivion[®] membrane. An optimization of the catalytic ink composition was carried out, according to the different ionomers characteristics to be used in the catalytic layer in order to reduce the degradation level. The stability is assessed by considering the variations of the performance and electrochemical parameters, such as electrochemical surface area (ECSA) and mass activity (j_m), at the beginning and end of accelerated stress test procedures.

1. INTRODUCTION

Polymer electrolyte membrane fuel cells (PEMFCs) are very good candidates for the power generations in transportation, stationary and portable systems, due to high energy density and easy recharging¹⁻³. One of the main drawbacks limiting the effective commercialization of PEMFC-based systems is associated to long-term performance and durability⁴⁻⁶. The durability of an operating PEMFC is affected by many external factors such as humidification, temperature, cell voltage, impurities or contaminants in the feeds^{7,8}. Each external factor has a direct influence on the stability of the key components of PEMFC such as catalysts, membrane, electrodes and membrane-electrode assembly (MEA). Accordingly, to enhance the stability of the system, it is necessary to improve the durability of each key component in a wide range of operating conditions. In the last years, many efforts were devoted to improve the stability at a higher working temperature and low relative humidity (RH), as required by the automotive fuel cell market^{9,10}. Unfortunately, in these operating conditions the used electro-catalysts and membranes are more subjected to issues related to the degradation and stability¹¹⁻¹³. In order to reduce the degradation phenomena of the electro-catalysts, several studies were addressed to use, instead of a pure Pt, binary and ternary Pt-alloys, such as PtCo, PtNi, PtCoCr, PtCoMn, PtNiMo¹⁴⁻²⁰. Moreover, many studies were devoted to use materials with reduced corrosion problems as a support of the metallic phase, such as carbon with different structures and high graphitic levels²¹⁻²⁴ or transition metals oxides²⁵⁻²⁸.

Regarding the membranes, not so many polymer electrolytes are able to operate with a constant performance in drastic conditions required for automotive applications. One of the most suitable polymer is Aquivion[®], a perfluorosulfonic electrolyte with a

short side chain developed by Solvay Specialty Polymers ²⁹. By changing the characteristics of the electrocatalysts and ionomers composing the catalytic layer of the electrodes, an optimization of the catalytic ink is required in terms of ionomer amount, used solvents, thermal treatment, etc. ³⁰. This is requested to achieve an optimal electronic and ionic percolation, high electrocatalytic activities and proper mass transport rates within the catalytic layer, and to ensure a higher stability of the MEAs during the time.

In our previous work ³¹, good performance and stability, for developed 50 wt% Pt (Pt/KB) and PtCo supported on Ketjenblack (PtCo/KB), were demonstrated in drastic operating conditions of temperature (110-130°C) and fully hydrated reactant gas, by using long (Nafion[®] 1100) and short (Aquivion[®] 790) side chain polymer based membranes. Moreover, the developed Pt/KB electrocatalyst showed a better performance, in similar operating conditions, when Aquivion[®] ionomer and membrane were used ²⁹.

In this work, the promising PtCo/KB and Pt/KB electrocatalysts were investigated with the aim of verifying the performance and stability, coupling them with an innovative reinforced Aquivion[®] membrane. An optimization of the catalytic ink composition was carried out according to the different ionomers characteristics to be used in the catalytic layer in order to reduce the degradation level. The degradation tests were performed at $T_{\text{cell}}=80^{\circ}\text{C}$ and 50% RH, in agreement with the new EU document on the test protocols for automotive applications ³², aimed at obtaining an unified set of harmonized conditions to test the MEAs.

EXPERIMENTAL SECTION

Catalysts preparation and characterisation

The cathode catalyst consisted of a 50 wt % PtCo, supported on Ketjenblack EC (PtCo/KB) with a nominal alloy composition of Pt₃Co₁ (at.) and prepared by an incipient wetness of cobalt nitrate on an amorphous PtOx/C catalyst. The corresponding Pt loading was 47.5 wt %. The detailed procedure was reported elsewhere⁹. The anode catalyst was a 50 wt % Pt/KB. This catalyst was prepared according to a previous work. The resulting powders were characterized by transmission electron microscopy (TEM, Philips CM12 microscope) and X-ray diffraction (XRD, Philips Xpert 3710 X-ray diffractometer with Cu K α radiation operating at 40 kV and 20 mA) to confirm the morphology and the crystallographic structure.

Membranes and ionomers preparation

The membrane used in this work is an experimental Aquivion[®] reinforced membrane developed from Solvay Specialty Polymers. The membrane (10 μ m in thickness) was prepared by ePTFE web impregnation starting from the commercially available Aquivion[®] PFSA D79-25BS water-based dispersion. A three-layered structure membrane with a smooth surface and tight interpenetration between the support and ionomer was obtained. Membrane manufacturing process was reported elsewhere³³. ~~In Figure 1 SEM image of the membrane cross section is reported for a better visualisation of the three layers.~~

Figure 1

Regarding the ionomer, three different dispersions were used differing in the equivalent weight (EW) and dispersant solvent. The first one is D79-25BS with an EW: 790 g/mol

and water as a dispersant; the other two ionomers, D83-06A and D83-25BS, having an EW of 830 g/mol, higher than the previous one, were dispersed in different solvents: hydro-alcoholic solution for the former and water for the latter. A Nafion[®] commercial membrane, NR212 by Ion Power, and Nafion hydro-alcoholic dispersion LQ1105 by Ion Power, were used as material for electrocatalysts comparison.

Electrodes and MEAs Preparation

Self-made electrodes were prepared by spraying the catalytic ink onto the commercial gas diffusion layer Sigracet-25BC (SGL group)³⁰. The catalytic ink was obtained by mixing the developed catalysts and a 26 wt % of Aquivion[®] ionomer dispersions, or a 33 wt % of Nafion[®] LQ1105 ionomer. In addition, a 20 wt % of ammonium carbonate (Carlo Erba) was used as a pore-former. A Pt loading of 0.2 mg cm⁻² both for the anode and cathode side was used. The prepared electrodes were subjected to a thermal treatment in an oven at 70°C and 125°C for 30 minutes for each step.

Membrane-Electrode Assemblies (MEAs) were obtained by hot pressing the electrodes onto the membranes, at 125°C with a pressure of 20 kgcm⁻² for 5 minutes. The membranes were used as received without any further treatments.

MEAs were prepared by coupling the anodic catalyst (50 wt.% Pt/KB) with the cathodic catalyst (50 wt.% PtCo/KB) and compared to MEAs containing a commercial 40 wt.% Pt/C (HiSPEC[®] 4000, Alfa Aesar) electrocatalyst, both for the anode and for the cathode, used as a benchmark. In Table 1, a summary of the realized MEAs is reported.

Table 1

Electrochemical Tests

Electrochemical tests were performed in a 25 cm² single cell, at 80°C, by feeding the cell with H₂ at the anode and air or O₂ as an oxidant at the cathode. The flow rates were fixed at 2 and 1.5 times the stoichiometric value for oxidant and fuel, respectively. The single cell performance in terms of polarisation curve, was investigated by steady-state galvanostatic measurements. The cell was connected to a Fuel Cell Technologies test station including an HP6051A electronic load. An AUTOLAB Potentiostat/Galvanostat (Metrohm), equipped with a 20 A current booster, was used for electrochemical diagnostics in terms of cyclic voltammetry (CV) and linear sweep voltammetry (LSV). The CV studies, under PEMFC configuration, were carried out by feeding hydrogen to the anode that operated as both counter and reference electrode and nitrogen to the cathode (working electrode) at 1 bar abs. The potential was ranging between 20 and 1250 mV with a sweep rate of 50 mVs⁻¹. The Electrochemical Surface Area (ECSA) was determined by integrating the CV profile in the hydrogen adsorption region after a correction for the double layer capacitance.

The electrochemical H₂ crossover was determined by LSV, feeding hydrogen to the anode, which operated as both counter and reference electrode, and nitrogen to the cathode (working electrode). The potential scan was recorded between 0 and 800 mV, with a sweep rate of 4 mVs⁻¹.

Two different accelerated stress test procedures (AST1, AST2) were used with different purposes. AST1 was performed in H₂/O₂ at 80°C, 100% RH and 1.5 bar abs, by cycling the cell potential between 0.6 and 0.9 V for about 10⁴ cycles. Every cycle consisted of two steps of 5 seconds at the fixed cell potential, so each cycle had a duration of 10 seconds. In this case, MEA1 and MEA2, containing commercial and developed electrocatalysts respectively, coupled with Nafion[®] membrane were compared in order

to assess the electrocatalysts stability. AST2 consisted of a steady state experiment at the Open Circuit Voltage (OCV) value (for about 95 hours) at 80°C, 50% RH, 1.5 bar_{abs}, H₂/air, to evaluate the MEA stability with the innovative Aquivion[®] membrane as a function of the ionomer. In this case, MEAs 3-8 were tested and compared (Table 1). The performance analyses were carried out by comparing the polarisation curves, CV and LSV results at the beginning of test (BoT) and the end of test (EoT). Main parameters such as j_m (Catalytic Mass Activity), ECSA, V_{cell} @ 0.8 and 1.55 Acm⁻² for AST1 and OCV, ECSA, H₂ Crossover for AST2 were considered.

RESULTS AND DISCUSSION

Figure 1 shows the XRD patterns for the developed electrocatalysts (Pt/KB and PtCo/KB). The typical peaks of a face centred cubic structure (fcc) of Pt are evident for Pt/KB (Figure 1a). From the analysis of the (220) reflection, a crystallite size of 2.5 nm was determined. PtCo/KB catalyst (Figure 1b) presents a single ordered primitive cubic (L1₂) phase for the alloy; this is evident from the presence of the superlattice reflections such as (100), (110) and (210) and a matching with the JCPDS card (29-0499)⁹. By analysing the (220) reflection, a crystallite size of 3.3 nm was calculated.

Figure 1

TEM images, reported in Figure 2, highlight a good dispersion of the Pt particles (Figure 2a) and of the metallic PtCo (Figure 2b) alloy on the carbonaceous support. The particle size derived from TEM images is 2.8 nm for Pt/KB (Figure 2c) and 3.4 nm for PtCo/KB (Figure 2d), in accordance with the XRD data.

Figure 2

The performance and stability of developed electrocatalysts were investigated and compared to commercial catalysts. For this reason, MEA1 and MEA2, containing the Nafion[®] membrane and ionomer, were tested following the AST1 procedure. Figure 3 shows the I-V curves at the BoT and the EoT for MEA1 (Figure 3a) and MEA2 (Figure 3b) obtained following AST1.

Figure 3

No performance change was highlighted between the BoT and the EoT for PtCo/KB catalyst (MEA2). On the contrary, a decrease of voltage in the whole polarisation curve was observed for the commercial catalyst (MEA1). At EoT, for the MEA1, the activation region is almost unaltered, whereas the ohmic and diffusive regions are more affected by the degradation, as observed by a much higher slope of I-V curve compared to the BoT curve. In particular, a voltage loss of about 30 mV in the ohmic region and a performance decrease of about 70 mV in the diffusive region of the polarisation curve are recorded.

The main electrochemical parameters for the two cathode catalysts (benchmark Pt/C in MEA1 and PtCo/KB in MEA2) are reported in Table 2 in order to compare the durability of the electrocatalysts^{32,33}. PtCo/KB catalyst (MEA2) does not suffer any degradation phenomenon. In fact, both the ECSA value and V_{cell} at 0.8 and 1.55 Acm⁻² do not change from BoT to EoT. At the BoT, a lower mass activity and ECSA for the benchmark catalyst (MEA1) compared to PtCo/KB (MEA2) is evident. These

differences are more pronounced at the EoT, confirming a strong reduction of these electrochemical parameters, as reported in Table 2. At the EoT, PtCo/KB catalyst shows a higher mass activity (j_m) at 0.9 V, although the other parameters, such as ECSA, are almost unvaried. This could be attributed to a further cleaning of the surface from poorly alloyed Co⁹, which produces a more active surface for the oxygen reduction reaction^{36,37}. Moreover, from the XRD analysis, the same crystallite size (3.3 nm) was found after 10⁴ cycles.

On the contrary, the benchmark Pt/C catalyst (MEA1) shows a loss in ECSA of about 25% that produces a decrease of mass activity (16%). These results are in accordance with an increase of the crystallite size (from 3.5 nm to 4.5 nm), calculated by XRD, nevertheless they are within the durability targets^{34,35}. In addition, a more pronounced reduction of cell potential is noticed at 0.8 Acm⁻² (33 mV loss) and 1.55 Acm⁻² (50 mV loss).

Table 2

The lifetime of a PEMFC depends not only on the electrocatalysts stability, but also on the membrane, especially when drastic operating conditions (50% RH), such as for automotive application, are used. In this case, reinforced membranes with low EW are preferred to improve the mechanical and chemical resistance at low RH²⁹. The innovative reinforced Aquivion[®] membrane was developed for this aim, with a thin thickness (10 μ m) to improve the cell performance. To assess the stability of the MEAs based on the developed and commercial electrocatalysts coupled to the innovative

Aquivion[®] membrane, AST2 was carried out. In this case, the ionomer D79-25BS with the same EW of the membrane (790 gmol⁻¹) was utilised to prepare the catalyst ink. Figure 4 reports the behaviour of MEA3 and MEA6 as a function of the time.

Figure 4

Despite the initial OCV for the MEA based on commercial catalysts is higher than the OCV of MEA with the developed catalysts, the trend changes after about 50 hrs of test, demonstrating a better stability for MEA6.

In fact, a decay of 0.8 mVh⁻¹ was recorded for PtCo/KB (MEA6) versus a decay of 1.6 mVh⁻¹ for the benchmark catalyst (MEA3).

Similarly, an almost identical H₂ crossover value (from 4.0*10⁻⁸ at BoT to 4.6*10⁻⁸ mol s⁻¹ cm⁻² at EoT) and no variation in the ECSA value (36 m²g⁻¹) were observed after the test for the PtCo-based MEA (MEA6). On the contrary, an ECSA reduction of about 22% and a significant increase of H₂ crossover value (from 2.1*10⁻⁸ to 8.6*10⁻⁷ mol s⁻¹ cm⁻²) were found for MEA3, equipped with the benchmark catalysts. This effect could be attributed to the Co in the catalyst that acts as a scavenger, mitigating the formation of the peroxide radicals that could produce a degradation of the ionomer in the catalytic layer and in the membrane^{38,39}. The obtained results confirm a better stability for MEA6, based on PtCo/KB.

In order to evaluate the influence of the ionomer features on the catalytic layer, AST2 was carried out on the MEAs based on Aquivion[®] ionomers, D83-25BS and D83-06A, having a higher EW than the previous one (D79-25BS), and dispersed in different solvents (see experimental part). The comparison between the commercial and developed electrocatalysts was carried out separately. In Figure 5 AST2 results related to benchmark-catalyst-based MEAs (MEAs 3-5) are reported.

Figure 5

MEAs with a higher EW ionomers (D83-25BS and D83-06A) show a more uniform decay during the test duration. In any case, a greater instability was recorded for D83-25BS (MEA4), as evident in Figure 5 due to the higher potential oscillations, especially after 50 hours of test. A decay of 1.2 mVh^{-1} was recorded for D83-06A (MEA5) versus a decay of 1.7 mVh^{-1} for D83-25BS (MEA4); as already reported, 1.6 mVh^{-1} was registered for D79-25BS (MEA3). This indicates a better MEA stability by using the D83-06A ionomer in the catalytic layer. The electrochemical data at the BoT and EoT are reported in Table 3. When the same solvent dispersant (water as in MEA3 and MEA4 with D79-25BS and D83-25BS ionomers, respectively) is used, a higher loss of OCV, ECSA and larger H_2 crossover was recorded for ionomer with higher EW (D83-25BS), indicating that an ionomer with lower EW (D79-25BS in the present case) is more suitable to operate at low RH. By changing the ionomer dispersion, using water instead of alcohol (MEA4 vs. MEA5), the stability and the performance of the MEA improve. This is due to a better ionomer distribution in the catalytic layer and interaction with the catalyst.

Table 3

Similar tests were carried out with MEAs based on developed catalysts. Figure 6 shows the results related to the chronopotentiometric experiments carried out on these MEAs. Even in this case, a greater instability was recorded for D83-25BS (MEA7), as evidenced by a faster decrease of the potential with the time. As reported above, the MEA based on PtCo/KB cathode catalyst showed a better stability than the commercial

catalyst, in the experiment whereas the ionomer with low EW was used (Figure 4). A further improvement in MEA stability was achieved by using the in-house prepared catalysts and the most stable ionomer D83-06A.

Figure 6

The recorded decays were 0.7 mVh^{-1} for MEA8 (D83-06A ionomer), 1.4 mVh^{-1} for MEA7 (D83-25BS ionomer) and 0.8 mVh^{-1} for MEA6 (D79-25BS ionomer). Analysing the electrochemical parameters for the MEAs based on the developed catalysts, collected in Table 4, a behaviour of the employed ionomers analogous to that found for the benchmark catalysts was observed. Accordingly, the ionomer with high EW and water as a dispersant produces a worsening of MEA stability (MEA7), as highlighted by the ECSA reduction and H_2 -crossover increase. Instead, by using the hydroalcoholic ionomer dispersion (MEA8) a good stability for the MEA was verified. Moreover, a similar value of H_2 crossover between the BoT and EoT and a very low reduction of ECSA (from 51 to $43 \text{ m}^2 \text{ g}^{-1}$) were recorded for MEA8 after the AST2.

Table 4

Starting from these results, it is possible to hypothesise that the alcoholic ionomer (D83-06A) improves the catalyst utilisation. In fact, the alcoholic dispersion of the ionomer permits a more homogeneous distribution of the ionomer in the catalytic layer leading to obtain more active sites for the catalytic layer⁴⁰, especially when a carbon with a higher surface area was used as a catalyst support (KB). Moreover, if the MEAs with the same ionomer and different catalysts (MEA5 vs. MEA8) are compared, a lower decay during

the OCV test (8% vs. 13%) is obtained with the in-house catalysts, confirming the suitable stability of the developed materials. Furthermore, the performance and ECSA at the EoT are higher for MEA8, using in-house PtCo/KB, compared to MEA5, based on the commercial Pt/C. These results seem to be very promising taking also into account the very thin membrane (10 μm) used.

CONCLUSIONS

In this work, an investigation of the MEA stability by using in house developed electrocatalysts, Aquivion[®] membrane and ionomers was carried out. In particular, the MEAs equipped with PtCo/KB cathode catalyst were subjected to accelerated stress tests and compared to benchmark Pt/C catalyst. It was found that the MEA with PtCo/KB catalyst showed superior durability compared to the MEA based on Pt/C.

In addition, it was found that an improvement of the MEA stability could be obtained by changing the characteristics of the ionomer used in the catalytic layer. In particular, the catalytic layer with a high EW (830 meq/mol) showed a higher degradation resistance than the ionomer with a lower EW (790 meq/mol) during the accelerated stress test at OCV (AST2). The optimised MEA based on in-house developed electrocatalysts (PtCo/KB and Pt/KB) and D83-06A (EW830 meq/mol) ionomer in the electrodic structure (MEA8) presents a limited increase of H₂-crossover, maintaining a higher performance and a higher ECSA value after the AST2. This behaviour was attributed to the presence of Co in the electrocatalyst, which acts as a scavenger and to a more homogeneous distribution of the ionomer in the catalytic layer, due to the alcoholic dispersion of the ionomer.

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Figure 1: XRD patterns for (a) Pt/KB and (b) PtCo/KB electrocatalysts.

Figure 2: TEM images and particle size distribution for Pt/KB (a,c) and PtCo/KB (b,d)

Figure 3. I-V curves comparison at the BoT and EoT for the MEA1 (a) and MEA2 (b) at 80°C, H₂/O₂, 100% RH, 1.5 bar abs (AST1).

Figure 4. AST2 chronopotentiometric analyses for MEA3 and MEA6, at 80°C, H₂/air, 50% RH, 1.5 bar abs.

Figure 5. AST2 chronopotentiometric analyses for MEA3, MEA4 and MEA5, at 80°C, H₂/air, 50% RH, 1.5 bar abs

Figure 6. AST2 chronopotentiometric analyses for MEA6, MEA7 and MEA8, at 80°C, H₂/air, 50% RH, 1.5 bar abs

Table 1: MEAs realized by using benchmark materials or in-house developed catalysts, ionomers and membranes.

MEA	Anode Catalyst	Cathode Catalyst	Ionomer	Membrane
MEA1	Pt/C	Pt/C	Nafion	NR212
MEA2	Pt/KB	PtCo/KB	Nafion	NR212
MEA3	Pt/C	Pt/C	D79-25BS	Aquivion
MEA4	Pt/C	Pt/C	D83-25BS	Aquivion
MEA5	Pt/C	Pt/C	D83-06A	Aquivion
MEA6	Pt/KB	PtCo/KB	D79-25BS	Aquivion
MEA7	Pt/KB	PtCo/KB	D83-25BS	Aquivion
MEA8	Pt/KB	PtCo/KB	D83-06A	Aquivion

Table 2. MEA1 and MEA2 electrochemical parameters at 80°C H₂/O₂ and 100% RH.

Sample	BoL AST1				EoL AST1			
	j_m^* mA _{mg} ⁻¹	ECSA m ² g ⁻¹	$V_{cell}@0.8$ Acm ⁻²	$V_{cell}@1.55$ Acm ⁻²	j_m^* mA _{mg} ⁻¹	ECSA m ² g ⁻¹	$V_{cell}@0.8$ Acm ⁻²	$V_{cell}@1.55$ Acm ⁻²
Pt/C (MEA1)	106	40	0.694	0.578	89	30	0.661	0.528
PtCo/KB (MEA2)	118	44	0.678	0.545	155	44	0.678	0.545

*IR_{free} @ 0.9 V

Table 3. MEAs3-5 electrochemical parameters at 80°C and 50% RH in H₂/air.

Sample	BoL OCV	EOl OCV	BoL ECSA, m ² g ⁻¹	EOl ECSA, m ² g ⁻¹	BoL H ₂ crossover, mol s ⁻¹ cm ⁻²	EOl H ₂ crossover, mol s ⁻¹ cm ⁻²	BoL V _{cell} @0.8 Acm ⁻²	EOl V _{cell} @0.8 Acm ⁻²
MEA3	0.910	0.777	36	28	2.1*10 ⁻⁸	8.6*10 ⁻⁷	0.611	0.528
MEA4	0.916	0.767	35	24	8.1*10 ⁻⁹	2.1*10 ⁻⁷	0.667	0.584
MEA5	0.910	0.794	35	35	5.7*10 ⁻⁹	2.1*10 ⁻⁸	0.678	0.617

Table 4. MEAs 6-8 Electrochemical parameters at 80°C and 50% RH in H₂/air.

Sample	BoL OCV	EoL OCV	BoL ECSA, m ² g ⁻¹	EoL ECSA, m ² g ⁻¹	BoL H ₂ crossover, mol s ⁻¹ cm ⁻²	EoL H ₂ crossover, mol s ⁻¹ cm ⁻²	BoL V _{cell} @0.8 Acm ⁻²	EoL V _{cell} @0.8 Acm ⁻²
MEA6	0.900	0.810	36	36	4.0*10 ⁻⁸	4.6*10 ⁻⁸	0.528	0.512
MEA7	0.916	0.783	32	23	9.1*10 ⁻⁹	1.5*10 ⁻⁸	0.634	0.485
MEA8	0.932	0.850	51	43	9.7*10 ⁻⁹	1.3*10 ⁻⁸	0.684	0.623

HIGHLIGHTS

- MEA with PtCo/KB catalyst shows superior durability compared to Pt/C
- CL with ionomer with EW830 has higher degradation resistance than with EW790
- Optimised MEA maintains higher performance and ECSA after AST

(a)

(b)

Figure 1

(a)

(b)

(c)

(d)

Figure 2

Figure 3

Figure 4

Figure 5

Figure 6